MERCURY AND AIR TOXIC ELEMENT IMPACTS OF COAL COMBUSTION BY-PRODUCT DISPOSAL AND UTILIZATION

Quarterly Technical Report

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ABSTRACT

This quarterly report summarizes the efforts and accomplishments related to investigations of releases of mercury and other air toxic elements from coal combustion by-products (CCBs). This report focuses on laboratory efforts related to the characterization of CCBs, long-term ambient-temperature release experiments, real-time mercury vapor thermal desorption, and microbiologically mediated release experiments. Data are presented for a variety of samples evaluated, including a few baseline/mercury control testing sample sets. Mercury release data are presented for the initial collection period of the third set of long-term ambient-release experiments. Additional results for the previous microbiologically mediated release data are presented. Data generated during this quarter are under review. Technology transfer efforts continued.

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LIST OF ACRONYMS

CCB	coal combustion by-product
DOE	U.S. Department of Energy
EERC	Energy & Environmental Research Center
FGD	flue gas desulfurization
LOI	loss on ignition
LTL	long-term leaching
NETL	National Energy Technology Laboratory
SDA	spray dryer absorber

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EXECUTIVE SUMMARY

New fly ash and flue gas desulfurization samples obtained this quarter included a mercury control test fly ash sample that is paired with a previously obtained baseline sample. All new samples helped fill gaps in the project sample set.

Generation of mercury thermal desorption curves continued, and interpretation of these curves was a major focus of this quarter. A new long-term ambient-temperature release experiment was initiated with ten samples in duplicate, and initial mercury releases were measured. A microbiological release experiment was initiated but the high alkalinity of the samples prevented continuous neutralization and killed the bacteria, preventing analyses. Long-term leaching of paired baseline and mercury control testing samples continued. In addition, analyses for pH, moisture content, and loss on ignition are presented along with mercury and air toxic element leachate analyses from the previous microbiological release experiment.

A presentation was given by Debra Pflughoeft-Hassett at the U.S. Department of Energy (DOE) National Energy Technology Laboratory Mercury Control Technology R&D Program Review held July 12–14, 2005, in Pittsburgh, Pennsylvania. David Hassett and Debra Pflughoeft-Hassett coordinated the "Mercury and Coal Utilization By-Products" session at the Air Quality V International Conference held September 19–21, 2005, in Arlington, Virginia. Mercury- and air toxic element-related papers collected during this quarter were added to the Mercury and Air Toxic Element Database located on the Coal Ash Resource Center Web site at www.undeerc.org/carrc/mercury.

A no-cost extension of the project was proposed to DOE and all project partners, which will extend the project from January to September 2006. This extension will allow researchers sufficient time to evaluate recently received sample types that had previously been missing from the project sample set.

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INTRODUCTION

This effort focuses on the evaluation of coal combustion by-products (CCBs) for their potential to release mercury and other air toxic elements under different controlled laboratory conditions and will investigate the release of these same air toxic elements in select disposal and utilization field settings to understand the impact of various emission control technologies. Information will be collected, evaluated, and interpreted together with past Energy & Environmental Research Center (EERC) and similar data from other studies. Results will be used to determine if mercury release from CCBs, both as currently produced and as produced with mercury and other emission controls in place, will potentially impact CCB management practices. The project will provide data on the environmental acceptability of CCBs expected to be produced in systems with emission controls for typical disposal and utilization scenarios. The project will develop baseline information on the release mechanisms of select elements in both conventional and modified or experimental CCBs. The modified or experimental CCBs will represent those from systems that have improved emission controls. Controlling these emissions has a high potential to change the chemical characteristics and environmental performance of CCBs. Development of reliable methods to determine the release of mercury from CCBs will provide a means of evaluating the environmental risk associated with CCB management practices. Using appropriate methods to develop data about currently produced CCBs and those produced under experimental or simulated conditions will provide a baseline for the CCB industry to understand the impact of various emission control technologies.

A no-cost extension of the project was proposed to the U.S. Department of Energy (DOE) and all project partners, which will extend the project from January to September 2006. This extension will allow researchers sufficient time to evaluate recently received sample types that had previously been missing from the project sample set.

EXPERIMENTAL

Literature Search

Researchers continued to collect publications related to mercury, air toxic elements, and CCBs. Citations and abstracts were assembled and added to the Mercury and Air Toxic Element document database located at www.undeerc.org/carrc/mercury. This database is password-protected and only available to project researchers and sponsors.

Analytical Methods Selection

No activity this quarter.

Sample Identification and Selection

Flue gas desulfurization (FGD) material and fly ash samples were received. One fly ash sample was a mercury control testing sample that is paired with a baseline sample received previously.

Chemical and Physical Characterization

Distilled-water pH values of five CCBs were determined. Moisture content and loss on ignition (LOI) were determined on 15 samples.

Laboratory Evaluation of Air Toxic Element Release

Leaching

Long-term leachings (LTL) with 30- and 60-day equilibration times were initiated on six samples, consisting of paired baseline and mercury control testing sample sets. The 30-day LTL was completed on these samples.

Vapor Transport

The third batch of long-term ambient-temperature mercury release experiments was initiated. All samples were set up in duplicate; however, Sample 03-082 was set up in duplicate with extra tubes containing Carbotrap™ added to capture any potential organomercury species as well as in duplicate in the same manner as the other samples. The 7-day releases from all of the samples were measured. The first 45-day releases from select samples were measured.

Sample 03-082 was also included in the second batch of long-term ambient-temperature mercury release experiments. Mercury release collection continued beyond that of the remaining samples in the set to establish a continuing trend of release. Water was present on the top of the sample at the beginning of the experiment, and this water evaporated during the experiment.

Mercury thermal desorption curves were generated for numerous samples by atomic absorption.

Microbiological Release

An experiment was initiated to evaluate four samples (Table 1) under aerobic and anaerobic glucose-fed conditions in triplicate. The latest method was varied slightly. An 18-g (instead of 20-g) sample, a 135-mL (instead of 150-mL) buffer solution, and a 100-µL aliquot of a sulfate-reducing bacteria culture were used for evaluation. The sample and buffer aliquots were reduced to allow for more sulfuric acid, but the ratio of sample to buffer solution was maintained. A sample-dependent amount of sulfuric acid was added over an extended period of time instead of within 1 day. The bacteria were added after the addition of the buffer and acid to allow the systems to neutralize. The system was stirred intermittently over the duration of the experiment.

Table 1. Samples Included in Microbiological Release Experiment

ID No.	Sample Type	Mercury Control	Total Hg, µg/g
04-035	Fly ash	No	0.160
04-036	Fly ash	Yes	0.287
05-001	Fly ash	No	0.004
05-003	Fly ash	Yes	0.565

The samples evaluated consisted of two paired sample sets, collected before and during mercury control testing. Samples 04-035 and 04-036 were repeated from the previous experiment because the pH had risen above the acceptable pH range for bacterial survival by the end of the previous experiment.

Field Investigation

Discussions about the Year 3 field investigation task continued. Options for field sites and potential simulated field sites are under consideration.

Data Reduction and Interpretation

Data assembly continued as laboratory results became available during the quarter. Assembly of vapor-phase release results to date was the focus of this task.

Technology Transfer

A presentation was given by Debra Pflughoeft-Hassett at the DOE National Energy Technology Laboratory (NETL) Mercury Control Technology R&D Program Review held July 12–14, 2005, in Pittsburgh, Pennsylvania. David Hassett and Debra Pflughoeft-Hassett coordinated the "Mercury and Coal Utilization By-Products" session at the Air Quality V International Conference held September 19–21, 2005, in Arlington, Virginia. Mercury- and air toxic element-related papers collected during this quarter were added to the Mercury and Air Toxic Element Database located on the Coal Ash Resource Center Web site at www.undeerc.org/carrc/mercury.

RESULTS AND DISCUSSION

Literature Search

This quarter, 11 documents were added to the Mercury and Air Toxic Element Database, which now contains 453 documents.

Analytical Methods Selection

No activity this quarter.

Sample Identification and Selection

The samples received this quarter increased the number of paired sample sets and FGD samples in the project. Work continued to access samples of value to the project. It is anticipated that new samples will be accepted through the next quarter.

Chemical and Physical Characterization

Table 2 shows the pH values for five CCBs using distilled water. Table 3 shows the moisture content and LOI for 15 CCB samples analyzed this quarter.

Table 2. CCB pH Values

ID No.	Sample Type	Mercury Control	pH
05-009	FGD gypsum	No	8.83
05-010	Fly ash	No	12.11
05-017	Fly ash	Yes	12.19
05-018	Fly ash	No	7.56
05-020	Fixated scrubber sludge	No	12.75

Table 3. Moisture Content and LOI, %

ID No.	Sample Type	Mercury Control	Moisture Content	LOI
02-002	Fly ash	Yes	5.56	22.2
02-003	Fly ash	Yes	2.92	19.4
02-004	Fly ash	Yes	0.53	2.84
02-007	Fly ash	Yes	4.63	23.9
02-069	Fly ash	Yes	0.86	12.6
02-070	Fly ash	No	0.24	5.88
02-072	Fly ash	No	0.21	5.39
02-074	Fly ash	No	0.36	6.27
02-076	Fly ash	Yes	0.60	21.1
03-005	Fly ash	No	0.18	3.60
05-009	FGD gypsum	No	26.0	1.92
05-010	Fly ash	No	0.33	2.05
05-017	Fly ash	Yes	0.05	1.70
05-018	Fly ash	No	0.04	3.01
05-020	Fixated scrubber sludge	No	31.09	3.65

Laboratory Evaluation of Air Toxic Element Release

Leaching

No leachate results were generated this quarter.

Vapor Transport

Results of the initial 7-day period of release in the long-term ambient-temperature mercury release experiment are shown in Table 4. The 7-day release results were used to determine which samples should be evaluated at a 45-day release period instead of the scheduled 90-day period for analytical reasons. Samples 03-082 and 05-009 exhibited higher 7-day releases and thus were analyzed at the 45-day period (Table 5).

Table 4. Ambient-Temperature Mercury Release in Initial 7-day Period, pg/g/day

ID No.	Sample Type	Mercury Control	Bottle 1	Bottle 2
03-065	FGD gypsum	No	0.0109	0.0133
03-082a	FGD filter cake	No	0.00876	0.271
03-082b	FGD filter cake	No	0.236	0.0331
04-029	Fly ash	No	0.00029	0.00055
04-038	Fly ash	No	0.00105	0.00076
04-044	Fly ash	No	<0.00001	0.00038
05-001	Fly ash	No	<0.00001	0.00035
05-002	Fly ash + FGD–SDA[a]	No	0.00040	0.00072
05-003	Fly ash	Yes	0.00031	0.00036
05-004	Fly ash + FGD–SDA	Yes	0.00037	<0.00001
05-009	FGD gypsum	No	0.0413	0.0392

[a] Spray dryer absorber ash.

Table 5. Ambient-Temperature Mercury Release in First 45-day Period for Select Samples, pg/g/day

ID No.	Sample Type	Mercury Control	Bottle 1	Bottle 2
03-082a	FGD filter cake	No	0.937	2.35
03-082b	FGD filter cake	No	4.14	3.77
05-009	FGD gypsum	No	0.0498	0.0407

Sample 03-082 has been evaluated for mercury release twice since the completion of the remaining samples in the second batch. This sample was evaluated at 57 days because the fifth 45-day period was missed, and it was tested again at 33 days in place of the sixth 45-day period to complete the 90-day period. Results are shown in Table 6. The release of mercury (pg/g/day) seems to be decreasing.

Table 6. Ambient-Temperature Mercury Release in Third 90-day Period for the Continuation of Second Batch Sample 03-082, pg/g/day

ID No.	Sample Type	Mercury Control	45-day Period	Actual Days	Bottle 1	Bottle 2
03-082	FGD filter cake	No	Fifth	57	2.51	1.69
03-082	FGD filter cake	No	Sixth	33	1.63	0.831

Mercury thermal desorption curves were generated for the 11 samples listed in Table 7, with the number of runs indicated. Interpretation of replicate runs is under way.

Table 7. CCB Samples Tested for Mercury Thermal Desorption

ID No.	Sample Type	Mercury Control	Runs
02-003	Fly ash	Yes	1
02-004	Fly ash	Yes	1
02-006	Fly ash	Yes	1
02-007	Fly ash	Yes	1
03-014	Fly ash	Yes	2
03-075	Fly ash	No	2
04-033	Fly ash	Yes	2
05-001	Fly ash	No	2
05-010	Fly ash	No	2
05-017	Fly ash	Yes	5
05-018	Fly ash	No	2

Microbiological Release

Analyses of samples generated in the previous experiment continued this quarter. The samples included in the previous experiment were 03-082, 04-035, and 04-036. Bacterial count evaluations indicated that sulfate-reducing bacteria were present in all samples of 03-082. Heavy bacterial growth was noted in the aerobic set of Sample 03-082. No bacteria were present for Samples 04-035 and 04-036 under both aerobic and anaerobic conditions. This confirms that the excessive pH levels noted at the end of the experiment killed the bacteria that were present in Samples 04-035 and 04-036. Results of leachate mercury and air toxic element concentrations are found in Table 8. The leachate from Samples 04-035 and 04-036 was not tested because of the excessive pH levels. Reevaluation of these samples was anticipated. The microbiological buffer was tested for the same elements (Table 9).

Table 8. Microbiological Leached Total Trace Element Results, µg/L

Anaerobic								Aerobic							
ID No.	As	Cd	Cr	Pb	Hg	Ni	Se	ID No.	As	Cd	Cr	Pb	Hg	Ni	Se
03-082	56	0.36	15	<2.0	0.034	22	23	03-082	14	0.35	13	<2.0	0.018	28	26
03-082	7.9	0.32	14	<2.0	0.041	16	3.8	03-082	19	0.35	15	<2.0	0.014	39	34
03-082	96	0.31	16	<2.0	0.036	18	22	03-082	26	0.34	13	<2.0	0.037	22	30
04-035	NT*	NT	NT	NT	NT	NT	NT	NT	04-035	NT	NT	NT	NT	NT	NT	NT
04-036	NT	NT	NT	NT	NT	NT	NT	NT	04-036	NT	NT	NT	NT	NT	NT	NT

* Not tested.

Table 9. Microbiological Buffer Total Trace Element Results, µg/L

Element	As	Cd	Cr	Pb	Hg	Ni	Se
Concentration	<2.0	0.41	18	<2.0	<0.01	<2.0	<2.0

Acid addition over an extended period was attempted to maintain an acceptable pH level over the duration of the last 30-day experiment. However, the pH of an aerobic sample measured 10.5 at the 20-day mark, which was significantly above the acceptable range of 6.5–8.5 for bacterial survival. The pH of all samples exceeded 10.5, which killed the bacteria. A pH adjustment of all samples was attempted for reinoculation of bacteria but was unsuccessful.

Field Investigation

Discussions of potential sites or alternative options for field testing continued. With the project extension to September 2006, field investigations are tentatively scheduled for spring 2006.

Data Reduction and Interpretation

Data interpretation was a focus for the preparation of a vapor-phase release topical report.

PLANS FOR NEXT QUARTER

During the next quarter, laboratory activities will continue. Characterization of samples will continue with moisture, LOI, and total mercury. Laboratory experiments will also include the leaching for the DOE NETL informal interlaboratory comparison on leaching procedures, standard leaching on new samples as-received, ambient-temperature vapor-phase release experiments, and microbiologically mediated mercury release experiments. A new buffer system will be evaluated for the highly alkaline samples in the microbiological experiment. Analytical activities on samples generated from the release experiments will continue as samples are generated.

Topical reports of vapor-phase release data and microbiological release data will be assembled and submitted to project sponsors.